## An Electrochemical Method to Visualize Flow and Measure Diffusivity in Liquid Metals

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## Objectives

The main objective of this program is to develop and demonstrate a novel electrochemical sensor for determining the fluid dynamic state in low Prandtl number, opaque liquid metals at high temperature. The basic idea is to use solid state electrochemical cells constructed at the container boundaries to control and detect the concentration of a tracer species. In this project, yttria stabilized zirconia (YSZ) is used as a solid oxygen-ion-conducting electrolyte and separates a 'working' liquid metal electrode from a 'reference' electrode. Atomic oxygen, dissolved in the liquid metal at the ppm concentration level, is detected by electrochemical cells operating in the galvanic mode. The same cell configuration is also used to establish localized concentration boundary conditions through coulometric titration of oxygen. Information about the dynamic state of the liquid metal is then obtained by perturbing the oxygen distribution in the liquid and observing the dynamic response of the measured EMF of the detection cells.

The magnitude of convective velocities encountered in the microgravity processing of liquid metals (e.g., bulk crystal growth of semiconductors) can be comparable to diffusive velocities. Thus accurate values of the oxygen diffusivity are necessary to separate the diffusive component of the oxygen flux from the convective component. Unfortunately, gravity driven convection in the melt prevents accurate measurement of the mass diffusivity of oxygen in liquid metal systems on earth. A second objective of this project is to perform the necessary ground-based investigations that will lead to the flight definition of a series of microgravity experiments to measure the temperature dependent diffusivity of oxygen in liquid metals. In addition to providing accurate values of the oxygen diffusivity for the flow visualization studies, these results should provide the research community with a benchmark for the development of improved ground-based cell configurations. Another science objective of this study is to establish the constitutive behavior of "Fickian" diffusion of oxygen in liquid metals.

## Need for Microgravity

The outcome of this research program will be a tool to experimentally determine the convective state in a contained liquid metal system. As such this tool should be useful to those performing microgravity research on a variety of processes including bulk crystal growth of compound semiconductors and the casting of metals.

Although a variety of methods have been used to study the fluid dynamics of high temperature, opaque liquid metal systems, many of these techniques are of low sensitivity, intrusive, or not easily adaptable to flight-based experimentation. In contrast, this tool is non-intrusive (the oxygen levels are typical of those present in liquid metal processing) and capable of detecting velocities as low as 10<sup>-4</sup> cm/sec. This technique is also highly adaptable to flight experimentation given power, weight, safety and signal level requirements. This method to visualize flow provides a fresh approach to a difficult problem that has the potential not only to enhance our understanding of the fluid dynamics of low Prandtl number fluids, but also provide a critical experimental link between computational fluid dynamics and processed material properties.

Both experimental and model results indicate that convection driven by solutal or thermal gradients is present in ground-based diffusivity experiments. These results include an order of magnitude increase in the measured diffusivity of oxygen in liquid tin when the solutal gradient is reversed in transient or steady state titration experiments and observations of changes in the measured diffusivity when varying the alignment of the cell axis with respect to the gravity vector or varying the aspect ratio of the cell. This should lead to flight measurements of the oxygen diffusivity in liquid metals to provide a benchmark for this popular electrochemical technique and give insight into the functional form of the diffusivity in liquid metals.

## Summary of Results

To explore the limits of this novel technique and to validate its robustness, a series of experiments have been designed using model fluids and geometries. Liquid Sn was selected as the model fluid because of its low vapor pressure and well defined thermophysical properties. Both cylindrical and rectangular geometries are being investigated experimentally as function of an imposed temperature gradient aspect ratio, and tilt. A technique was developed to locate YSZ sensors in the walls of alumina tubes to avoid the problem of ionic conduction within the wall that when using YS tubes. Successful experiments were performed in a cylindrical geometry to determine the flow orientation as a function of Ra and aspect ratio. Transitions from unicellular flow pattern to an axisymmetric flow configuration and to a stacked flow arrangement were observed upon increasing the aspect ratio. The observed flow patterns and estimated velocities were comparable to the predictions of Hardin et al. Additional experiments were performed with variable temperature gradients and measurement modes (e.g., pulsing input, galvanic or potentiostatic titration) to understand the limits of the technique. Oscillatory flow was recorded at high values of Ra.

Work was also initiated on measuring the convective flow in cylindrical geometries. Since very little modeling effort has been devoted to this geometry, 3-dimensional simulation studies were performed. Both steady (torroidal, unicellular, multiple cells) and oscillatory flow configurations were calculated depending on the aspect ratio and Ra. The tracer atomic Oxygen species balance was solved to allow a complete simulation of the electrochemical visualization technique. These simulations were used to design experiments which are now underway.

Coulometric titration procedures have long been used to determine values of the diffusivity of elements in liquid metals. The results of this study strongly indicate that convection driven by thermal or solutal gradients is present in most ground-based experiments. The measured values of the oxygen diffusivity depended on the cell size and experimental configuration. Measurements taken in configurations that gave rise to gravity driven convective flows also gave larger values of diffusion coefficients than measurements taken in configurations where the convective flows were apparently weaker. A detailed numerical model with a sophisticated 3-dimensional code was developed to predict the effects of imperfections such as tilts and radial heat losses. It concluded that even slight imperfections affect the diffusivity measurements for all of the cell configurations studied. For example, taller cells, which were associated with large time constants, increased the measurement error because of mass transfer through an overflow port to accommodate the expansion of tin upon heating. The initial oxygen concentration and cell dimensions both influenced the hydrostatic stability of the tin sample during a transient diffusion experiment. This is not surprising as the transport process is essentially the transient version of the Rayleigh-Bénard problem and the aspect ratio and Rayleigh number are two parameters which are found to define the stability criterion in that problem.

It is concluded that this novel technique holds considerable promise for use in a microgravity environment to detect low level flows and to accurately measure diffusivities. Furthermore, gravity driven convection in the melt prevents accurate measurement of the mass diffusivity of oxygen in metal systems by coulometric titration. This situation represents a clear example where a reduced gravity environment is necessary to obtain meaningful values of this important physical property.